Rising Arctic Ocean temperatures cause gas hydrate destabilization and ocean acidification

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[1] Vast amounts of methane hydrates are potentially stored in sediments along the continental margins, owing their stability to low temperature – high pressure conditions. Global warming could destabilize these hydrates and cause a release of methane (CH_4) into the water column and possibly the atmosphere. Since the Arctic has and will be warmed considerably, Arctic bottom water temperatures and their future evolution projected by a climate model were analyzed. The resulting warming is spatially inhomogeneous, with the strongest impact on shallow regions affected by Atlantic inflow. Within the next 100 years, the warming affects 25% of shallow and mid-depth regions containing methane hydrates. Release of methane from melting hydrates in these areas could enhance ocean acidification and oxygen depletion in the water column. The impact of methane release on global warming, however, would not be significant within the considered time span. **Citation:** Biastoch, A., et al. (2011), Rising Arctic Ocean temperatures cause gas hydrate destabilization and ocean acidification, *Geophys. Res. Lett.*, *38*, L08602, doi:10.1029/2011GL047222.

1. Introduction

[2] Formed under low temperature – high pressure conditions [*Tishchenko et al.*, 2005] vast amounts of methane hydrates are considered to be locked up in sediments of continental margins [*Buffett and Archer*, 2004; *Klauda and Sandler*, 2005]. In the Arctic Ocean (AO), hydrates are deposited at shallow water depths close to shelf edges, stabilized by year-round cold temperatures [*Hester and Brewer*, 2009]. Because the Arctic has warmed considerably during the recent decades and because climate models predict accelerated warming if global greenhouse gas emissions continue to rise [*Intergovernmental Panel on Climate Change* (*IPCC*), 2007], a destabilization of shallow Arctic hydrate deposits has been debated [*Reagan and Moridis*, 2007; *Kerr*, 2010]. Methane (CH_4), a gas with a global warming potential ~25 times higher than CO_2 [*IPCC*, 2007], could be released from the melting hydrates and enter the water column and atmosphere [*Krey et al.*, 2009]. Recent field studies indicate an increase in methane fluxes from submarine Arctic permafrost and the seafloor [*Westbrook et al.*, 2009; *Shakhova et al.*, 2010]. Our multi-disciplinary analysis provides a closer look into regional developments of submarine Arctic gas hydrate deposits under future global warming scenarios and reveals where and over which time scales gas hydrates could be destabilized and affect oceanic pH, oxygen, and atmospheric methane.

2. Temperature Evolution in the Mid-depth Arctic Ocean

[3] For an evaluation of the general distribution and the natural variability we investigated the spatio-temporal variability of Arctic bottom water in a hindcast experiment with the ocean/sea-ice model NEMO (v2.3) [*Madec*, 2006], carried out by the DRAKKAR collaboration [*The DRAKKAR Group*, 2007]. The global simulation was performed at 1/2° resolution (ORCA05) and 46 levels in the vertical, whereby partial bottom cells allowed realistic topographic slopes. The experiment, that demonstrated its fidelity in simulating the salient features of the Atlantic circulation variability [*Biastoch et al.*, 2008], was forced by inter-annually varying atmospheric boundary conditions of the past decades [*Large and Yeager*, 2004]. To exclude a potential model drift in the water masses a second experiment under repeated-year forcing was subtracted from the hindcast. The bottom water temperatures to first order reflect water depth (Figure 1a), featuring colder values around 0°C below 1000 m and warmer values on the shelves. However, a clear impact of the ocean circulation is seen as a band of temperatures around 1°C surrounding the AO at ~400 m, an expression of the Atlantic inflow below the Arctic halocline [*Polyakov et al.*, 2004]. Colder temperatures appear on the Russian and Canadian shelves due to the exposure of the surface waters to continental cold air outbreaks during winter.

[4] The Atlantic inflow from the European Nordic Seas (ENS) into the AO exhibits pronounced variability on decadal time scales [*Biastoch et al.*, 2008], following temperature and transport changes in the branch of the North Atlantic Current flowing through the ENS [*Holliday et al.*, 2008]. The flow of Atlantic water towards the AO south of Svalbard (Figure 2a) shows a remarkable consistency with observations, both in mean temperature (3.70 ± 0.60°C vs. 3.96 ± 0.69°C [*Holliday et al.*, 2008]) and variability, with minima in the late 1970s, mid 1980s and late 1990s. Changes towards warmer temperatures were reported for the past few decades [*Holliday et al.*, 2008], which are supported by the simulated long-term trend (0.014°C yr^{-1}). Although the long-term trend (<0.005°C yr^{-1}) of the bottom water is weaker (Figure 2b), a decadal variability by the Atlantic inflow is also present: changes over a single pentad repeatedly reach 0.75°C (red lines). The inflow signal extends to the shelf areas off Russia as part of the cyclonic circu-

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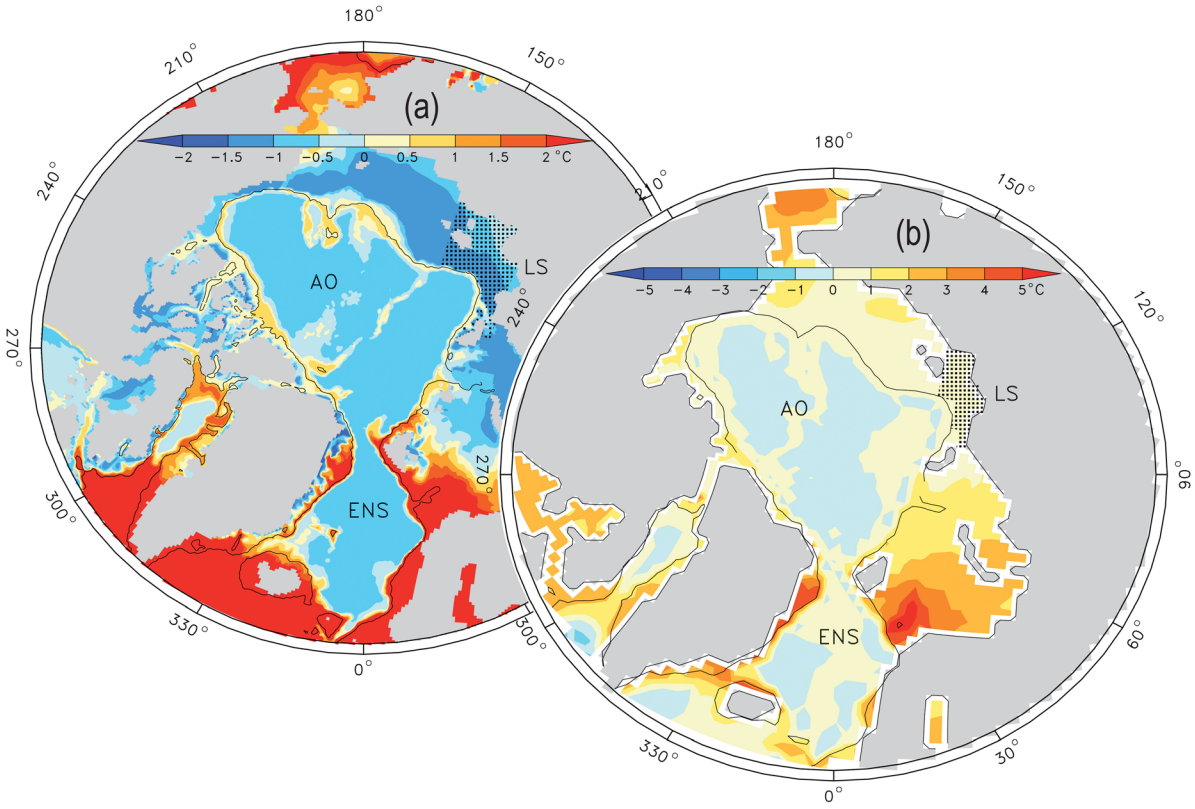

Figure 1. Map of the (a) time-mean (1985–2004) bottom water temperatures in the ocean hindcast simulation and (b) ensemble-mean trend in (in °C per 100 years) in the climate model simulation under CO_2 increase. The contour line depicts the 400 m isobath. The Laptev shelf area used for Figure 2c is marked by black stippling. Acronyms mark the Arctic Ocean (AO), European Nordic Seas (ENS) and the Laptev Sea (LS).

lation around the AO [*Dmitrenko et al.*, 2008]. Although the Arctic Intermediate Water also varies on a decadal time scale [*Polyakov et al.*, 2004], bottom water temperatures along the Russian slope remain almost unaffected (Figure 2c). Only the shallow and potentially methane-rich [*Shakhova et al.*, 2010] shelf regions in the Laptev Sea show significant annual variations.

[5] The future evolution of bottom water temperatures was analyzed in an ensemble of greenhouse warming integrations with a coupled climate model (KCM) [*Park et al.*, 2009]. This configuration utilizes the same numerical framework, but at lower resolution (ORCA2, 2° horizontally, 31 levels) and the atmospheric model ECHAM5 [*Roeckner et al.*, 2003] as an active atmosphere. In addition to a 430 year control experiment with present day greenhouse gas concentrations (CO_2 = 348 ppm), an ensemble of eight 100-year long global warming simulations, each starting from different states of the control run, were performed with 1% increase in the CO_2 equivalent concentration [*Park et al.*, 2009]. The linear trend of the ensemble average was combined with the ORCA05 distribution. The temperature changes (Figure 1b) show a highly inhomogeneous distribution, with increases of 1–2°C along the continental slopes and even higher values on the shelves due to the direct influence from the atmosphere. Individual ensemble members resembles strong inter-annual to decadal variability in the Nordic Seas (Figure S1 in Text S1 of the auxiliary material) due to different states of the Atlantic Ocean circulation, but all feature a consistent long-term trend of 2.5°C per century.[1] Anomalies take some decades to protrude into the Laptev Sea, depending on the state of the Arctic circulation [*Polyakov et al.*, 2004]; consistent trends are starting typically after 50 years.

3. Impact on Methane Hydrate Stability and Ocean Acidification

[6] Methane hydrate stability in marine sediments is mainly a function of temperature and pressure [*Tishchenko et al.*, 2005]. A thermodynamic analysis (Figure 3b) of selected Arctic regions illustrates that in the ENS the methane hydrate will experience a phase shift from hydrate to free gas in mid-depth levels at around 500 m within the next 100 years. Natural decadal variability can easily add another 0.75°C (Figure 2) to the long-term increase. Along the Russian slope only shallower depths (~300 m) undergo a phase shift.

[7] For the overall impact of future bottom water warming on the stability of methane hydrates potentially stored in the Arctic seafloor we explored the thickness of the gas hydrate

[1] Auxiliary materials are available in the HTML. doi:10.1029/2011GL047222.

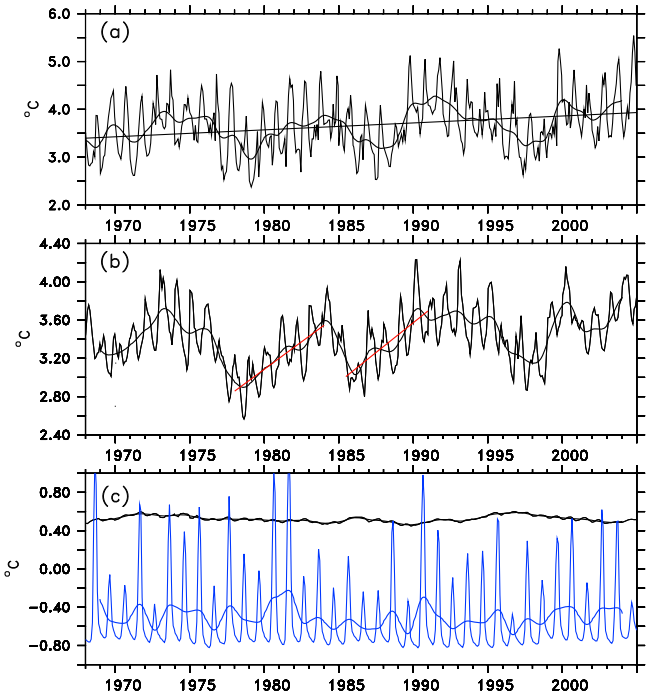

Figure 2. Variability of temperatures in the hindcast simulation, shown by monthly and inter-annually filtered temperatures of (a) the Atlantic inflow (50–200 m depth) off Svalbard and bottom water temperatures (b) along the eastern continental slope in the ENS off Svalbard and Norway (water depth 416–793 m) and (c) along the Russian continental slope, (black, 416–793 m, 90–180°E) and on the shelf (blue, 0–100 m) in the Laptev Sea. The red lines mark trends in particular 5-year periods.

stability zone (GHSZ) below the seafloor. The GHSZ is defined as that part of a sediment column where hydrostatic fluid pressures are higher than the temperature and salinity dependent dissociation pressure of gas hydrates. The dissociation pressure was calculated according to *Tishchenko et al.* [2005] using the fields from the ocean model and steady-state temperatures computed from global heat flow values in combination with an average sediment conductivity of 1.5 W m^{-1} K^{-1} for present (Figure S2) and future climates (Figure 3a). To roughly estimate the amount of hydrate within the GHSZ we used simple constant mean hydrate pore filling estimates of 2.4% (60–70°N) to 6.1% (north of 70°N) based on ODP data and numerical modeling [*Klauda and Sandler*, 2005]. Inhibition of hydrate formation by sulfate reduction is approximated by including a 5 m thick hydrate free zone below the seafloor. Assuming a mean porosity of 0.5 and standard values for density and methane content of hydrate, we estimated a total inventory of 900 Gt carbon (C) north of 60°N for the present climate. This value is not too far off the estimated 500 Gt C based on studies offshore Alaska [*Kvenvolden*, 1988] representing a fraction of the still largely unknown global hydrate inventory of 500–64,000 Gt C [*Hester and Brewer*, 2009]. Under the global warming scenario most affected regions are distributed around the AO and the ENS. Areas exhibiting decreases ≥20 m in the GHSZ thickness sum up to a total size of ~850,000 km^2 resulting in a total methane release of ~100 Gt C. However, these estimates are too high for the considered 100-year time window and need to be adjusted for the sluggish diffusion of heat into marine sediments. Using a constant thermal diffusivity of 4×10^7 m s^{-2} and neglecting the latent heat of hydrate melting, we find that only 12% of the worst-case hydrate volume is reduced after 100 years for sulfate reduction zone thicknesses 5 m (Figure 3c). Note that sensitivity runs with 0 and 10 m sulfate reduction zone thicknesses show reductions of 14 and 10%, respectively.

[8] What could happen to the released methane? It is conceivable from environmental hydrate studies that, depending on the release rate, at least ~50% of the methane that dissolves into the sediment porewater, could be retained inside the seafloor by microbial anaerobic oxidation of methane (AOM) [*Knittel and Boetius*, 2009; *Treude et al.*, 2003]. AOM represents a long-term sink for methane-derived carbon, converting methane into bicarbonate and eventually precipitating it as authigenic carbonates [*Peckmann et al.*, 2001]. However, methane rising through sediments as free gas could bypass the benthic methane filter [*Knittel and Boetius*, 2009] and, depending on water depth [*McGinnis et al.*, 2006], immediately reach the atmosphere. Methane that on the other hand dissolves into the water column could be utilized by microbial aerobic oxidation of methane [*Valentine et al.*, 2001]. Different to its counterpart AOM in sediments, aerobic oxidation of methane converts methane with oxygen into CO_2 – a molecule that can impact oceanic pH.

[9] For the following scenario we assume that 50% of the methane from the transient GHSZ thickness change is released into the water column and consumed by aerobic methanotrophs. A Lagrangian analysis of the oceanic currents (auxiliary material) shows that (within a given year) the bulk of the water affected by methane is kept within 100 m above the bottom and along the mid-depth topographic slope. Changes in seawater carbonate chemistry were calculated by adding the microbial produced CO_2 to the background dissolved inorganic carbon (auxiliary material). Some areas of the AO revealed pH values to drop by up to 0.25 units (Figure 4) within the next 100 years. Additionally, the aerobic consumption of methane could locally decrease bottom water oxygen concentrations by up to 25% (auxiliary material, data not shown). Regional methane-induced seawater acidification from the seafloor would occur in addition to an ocean-wide acidification caused by the uptake of anthropogenic CO_2 from the atmosphere [*IPCC*, 2007]. The combined effect of the two processes would accelerate ocean acidification in parts of the AO, including deeper waters which otherwise would be exposed to ocean acidification with a considerable time delay. Research on that topic so far has been conducted under the premises of a projected pH decrease due to the anthropogenic CO_2-uptake of about 0.3 units until the end of this century. Methane-induced acidification could nearly double this decrease in parts of the AO.

[10] If, in a rather unrealistic scenario, all of the liberated methane would reach the atmosphere, global warming could be amplified [*Bartdorff et al.*, 2008]. Under transient conditions we estimated an additional average methane flux of only 162 Mt CH_4 yr^{-1} from melting Arctic hydrates over the next 100 years (auxiliary material) – a value lower than the current anthropogenic input of (600 Mt yr^{-1}) [*Bartdorff et al.*, 2008]. Sensitivity experiments with the climate model confirm the negligible feedback of the climate system under

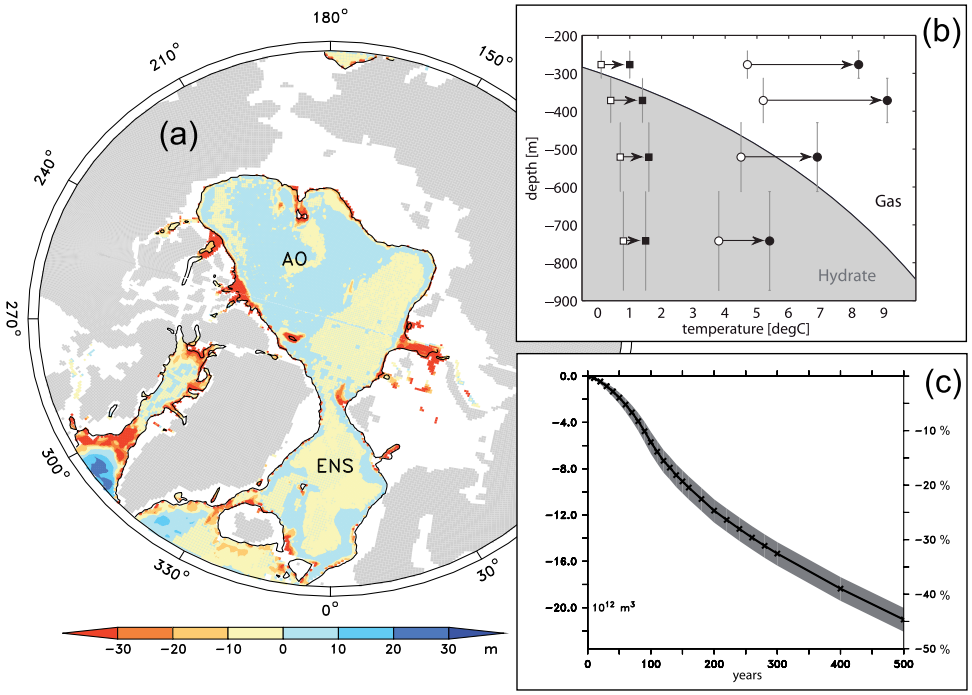

Figure 3. (a) Changes in thickness of the GHSZ caused by temperature increase of the ensemble mean of the global warming, (b) phase diagram of methane hydrate as a function of pressure and temperature (constant salinity of S = 35 p.s.u.). Open symbols mark the bottom water temperatures along the ENS (cycles) and Russian (squares) slopes in the present climate run, closed symbols the greenhouse warming experiments. Vertical bars indicate the vertical resolution of the ocean model. (c) Volumetric GHSZ thickness changes north of 60°N as a function of time. A value of 100% corresponds to the worst case scenario. The shaded range marks estimates for 0 and 10 m sulfate reduction zone thickness.

this limited additional amount of methane (Figure S3). On a longer time scale, however, the transient heat conduction leads to a faster methane release; the methane released from the steady-state GHSZ calculation causes an upper limit of 0.8°C increase in surface air temperature on top of global warming.

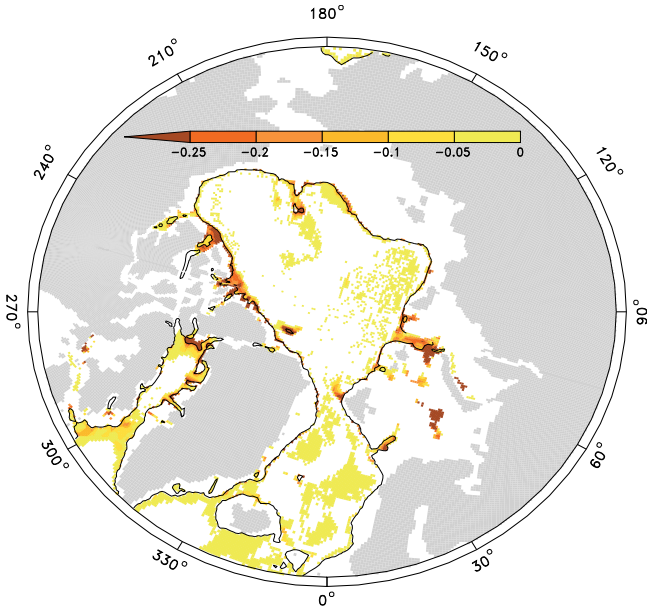

Figure 4. Changes in pH due to the release of 50% of the methane from hydrates within the first 100 years and distributed over the first 100 m above the bottom.

4. Conclusions

[11] The present study is to our knowledge the first combining ocean hindcasts and future climate projections with GHSZ calculations and potential consequences. It should be noted that the overall model still has its limitation with respect to the resolution of the bottom water temperatures, the actual distribution of sub-seafloor methane hydrates and the individual response of the microbial community in the sediment and water column. Nevertheless, the study clearly shows that hydrate destabilization can occur in the Arctic in response to global warming, and that the potential methane release is substantial, but limited in the next 100 years. An important finding is that warming and variability of the Atlantic inflow will play a major role in the fate of Arctic gas hydrates. Recent observations [*Westbrook et al.*, 2009; *Reagan and Moridis*, 2009] agree well with sensitive areas identified here. Our maps could represent a useful tool in identifying areas around the Arctic Ocean where increases in methane release are likely to occur now or in the near future.

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